

### 3.0 Methods, Issues, and Criteria for Measuring $K_d$ Values

There are 5 general methods used to measure  $K_d$  values: the batch laboratory method, laboratory flow-through (or column) method, field-batch method, field modeling method, and  $K_{oc}$  method. These methods and the associated technical issues are described in detail in Chapter 3 of Volume I. Each method has advantages and disadvantages, and perhaps more importantly, each method has its own set of assumptions for calculating  $K_d$  values from experimental data. Consequently, it is not only common, but expected that  $K_d$  values measured by different methods will produce different values.

#### 3.1 *Laboratory Batch Method*

Batch tests are commonly used to measure  $K_d$  values. The test is conducted by spiking a solution with the element of interest, mixing the spiked solution with a solid for a specified period of time, separating the solution from the solid, and measuring the concentration of the spiked element remaining in solution. The concentration of contaminant associated with the solid is determined by the difference between initial and final contaminant concentration. The primary advantage of the method is that such experiments can be completed quickly for a wide variety of elements and chemical environments. The primary disadvantage of the batch technique for measuring  $K_d$  is that it does not necessarily reproduce the chemical reaction conditions that take place in the real environment. For instance, in a soil column, water passes through at a finite rate and both reaction time and degree of mixing between water and soil can be much less than those occurring in a laboratory batch test. Consequently,  $K_d$  values from batch experiments can be high relative to the extent of sorption occurring in a real system, and thus result in an estimate of contaminant retardation that is too large. Another disadvantage of batch experiments is that they do not accurately simulate desorption of the radionuclides or contaminants from a contaminated soil or solid waste source. The  $K_d$  values are frequently used with the assumption that adsorption and desorption reactions are reversible. This assumption is contrary to most experimental observations that show that the desorption process is appreciably slower than the adsorption process, a phenomenon referred to as hysteresis. The rate of desorption may even go to zero, yet a significant mass of the contaminant remains sorbed on the soil. Thus, use of  $K_d$  values determined from batch adsorption tests in contaminant transport models is generally considered to provide estimates of contaminant remobilization (release) from soil that are too large (*i.e.*, estimates of contaminant retention that are too low).

#### 3.2 *Laboratory Flow-Through Method*

Flow-through column experiments are intended to provide a more realistic simulation of dynamic field conditions and to quantify the movement of contaminants relative to groundwater flow. It is the second most common method of determining  $K_d$  values. The basic experiment is completed by passing a liquid spiked with the contaminant of interest through a soil column. The column experiment combines the chemical effects of sorption and the hydrologic effects of groundwater flow through a porous medium to provide an estimate of retarded movement of the contaminant of interest. The retardation factor (a ratio

of the velocity of the contaminant to that of water) is measured directly from the experimental data. A  $K_d$  value can be calculated from the retardation factor. It is frequently useful to compare the back-calculated  $K_d$  value from these experiments with those derived directly from the batch experiments to evaluate the influence of limited interaction between solid and solution imposed by the flow-through system.

One potential advantage of the flow-through column studies is that the retardation factor can be inserted directly into the transport code. However, if the study site contains different hydrological conditions (*e.g.*, porosity and bulk density) than the column experiment, then a  $K_d$  value needs to be calculated from the retardation factor. Another advantage is that the column experiment provides a much closer approximation of the physical conditions and chemical processes occurring in the field site than a batch sorption experiment. Column experiments permit the investigation of the influence of limited spatial and temporal (nonequilibrium) contact between solute and solid have on contaminant retardation. Additionally, the influence of mobile colloid facilitated transport and partial saturation can be investigated. A third advantage is that both adsorption or desorption reactions can be studied. The predominance of 1 mechanism of adsorption or desorption over another cannot be predicted *a priori* and therefore generalizing the results from 1 set of laboratory experimental conditions to field conditions is never without some uncertainty. Ideally, flow-through column experiments would be used exclusively for determining  $K_d$  values, but equipment cost, time constraints, experimental complexity, and data reduction uncertainties discourage more extensive use.

### **3.3 Other Methods**

Less commonly used methods include the  $K_{oc}$  method, *in-situ* batch method, and the field modeling method. The  $K_{oc}$  method is a very effective indirect method of calculating  $K_d$  values, however, it is only applicable to organic compounds. The *in-situ* batch method requires that paired soil and groundwater samples be collected directly from the aquifer system being modeled and then measuring directly the amount of contaminant on the solid and liquid phases. The advantage of this approach is that the precise solution chemistry and solid phase mineralogy existing in the study site is used to measure the  $K_d$  value. However, this method is not used often because of the analytical problems associated with measuring the exchangeable fraction of contaminant on the solid phase. Finally, the field modeling method of calculating  $K_d$  values uses groundwater monitoring data and source term data to calculate a  $K_d$  value. One key drawback to this technique is that it is very model dependent. Because the calculated  $K_d$  value are model dependent and highly site specific, the  $K_d$  values must be used for contaminant transport calculations at other sites.

### **3.4 Issues**

A number of issues exist concerning the measurement of  $K_d$  values and the selection of  $K_d$  values from the literature. These issues include: using simple versus complex systems to measure  $K_d$  values, field variability, the “gravel issue,” and the “colloid issue.” Soils are a complex mixture containing solid,

gaseous, and liquid phases. Each phase contains several different constituents. The use of simplified systems containing single mineral phases and aqueous phases with 1 or 2 dissolved species has provided valuable paradigms for understanding sorption processes in more complex, natural systems. However, the  $K_d$  values generated from these simple systems are generally of little value for importing directly into transport models. Values for transport models should be generated from geologic materials from or similar to the study site. The “gravel issue” is the problem that transport modelers face when converting laboratory-derived  $K_d$  values based on experiments conducted with the <2-mm fraction into values that can be used in systems containing particles >2 mm in size. No standard methods exist to address this issue. There are many subsurface soils dominated by cobbles, gravel, or boulders. To base the  $K_d$  values on the <2-mm fraction, which may constitute only <1 percent of the soil volume but is the most chemically reactive fraction, would grossly overestimate the actual  $K_d$  of the aquifer. Two general approaches have been proposed to address this issue. The first is to assume that all particles >2-mm has a  $K_d = 0$  ml/g. Although this assumption is incorrect (*i.e.*, cobbles, gravel, and boulders do in fact sorb contaminants), the extent to which sorption occurs on these larger particles may be small. The second approach is to normalize laboratory-derived  $K_d$  values by soil surface area. Theoretically, this latter approach is more satisfying because it permits some sorption to occur on the >2-mm fraction and the extent of the sorption is proportional to the surface area. The underlying assumptions in this approach are that the mineralogy is similar in the less than 2- and greater than 2-mm fractions and that the sorption processes occurring in the smaller fraction are similar to those that occur in the larger fraction.

Spatial variability provides additional complexity to understanding and modeling contaminant retention to subsurface soils. The extent to which contaminants partition to soils changes as field mineralogy and chemistry change. Thus, a single  $K_d$  value is almost never sufficient for an entire study site and should change as chemically important environmental conditions change. Three approaches used to vary  $K_d$  values in transport codes are the  $K_d$  look-up table approach, the parametric- $K_d$  approach, and the mechanistic  $K_d$  approach. The extent to which these approaches are presently used and the ease of incorporating them into a flow model varies greatly. Parametric- $K_d$  values typically have limited environmental ranges of application. Mechanistic  $K_d$  values are limited to uniform solid and aqueous systems with little application to heterogeneous soils existing in nature. The easiest and the most common variable- $K_d$  model interfaced with transport codes is the look-up table. In  $K_d$  look-up tables, separate  $K_d$  values are assigned to a matrix of discrete categories defined by chemically important ancillary parameters. No single set of ancillary parameters, such as pH and soil texture, is universally appropriate for defining categories in  $K_d$  look-up tables. Instead, the ancillary parameters must vary in accordance to the geochemistry of the contaminant. It is essential to understand fully the criteria and process used for selecting the values incorporated in such a table. Differences in the criteria and process used to select  $K_d$  values can result in appreciable different  $K_d$  values. Examples are presented in this volume.

Contaminant transport models generally treat the subsurface environment as a 2-phase system in which contaminants are distributed between a mobile aqueous phase and an immobile solid phase (*e.g.*, soil).

An increasing body of evidence indicates that under some subsurface conditions, components of the solid phase may exist as colloids<sup>1</sup> that may be transported with the flowing water. Subsurface mobile colloids originate from (1) the dispersion of surface or subsurface soils, (2) decementation of secondary mineral phases, and (3) homogeneous precipitation of groundwater constituents. Association of contaminants with this additional mobile phase may enhance not only the amount of contaminant that is transported, but also the rate of contaminant transport. Most current approaches to predicting contaminant transport ignore this mechanism not because it is obscure or because the mathematical algorithms have not been developed, but because little information is available on the occurrence, the mineralogical properties, the physicochemical properties, or the conditions conducive to the generation of mobile colloids. There are 2 primary problems associated with studying colloid-facilitated transport of contaminants under natural conditions. First, it is difficult to collect colloids from the subsurface in a manner which minimizes or eliminates sampling artifacts. Secondly, it is difficult to unambiguously delineate between the contaminants in the mobile-aqueous and mobile-solid phases.

Often  $K_d$  values used in transport models are selected to provide a conservative estimate of contaminant migration or health effects. However, the same  $K_d$  value would not provide a conservative estimate for clean-up calculations. Conservatism for remediation calculations would tend to err on the side of underestimating the extent of contaminant desorption that would occur in the aquifer once pump-and-treat or soil flushing treatments commenced. Such an estimate would provide an upper limit to time, money, and work required to extract a contaminant from a soil. This would be accomplished by selecting a  $K_d$  from the upper range of literature values.

It is incumbent upon the transport modeler to understand the strengths and weaknesses of the different  $K_d$  methods, and perhaps more importantly, the underlying assumption of the methods in order to properly select  $K_d$  values from the literature. The  $K_d$  values reported in the literature for any given contaminant may vary by as much as 6 orders of magnitude. An understanding of the important geochemical processes and knowledge of the important ancillary parameters affecting the sorption chemistry of the contaminant of interest is necessary for selecting appropriate  $K_d$  value(s) for contaminant transport modeling.

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<sup>1</sup> A colloid is any fine-grained material, sometimes limited to the particle-size range of  $<0.00024$  mm (*i.e.*, smaller than clay size), that can be easily suspended (Bates and Jackson, 1980). In its original sense, the definition of a colloid included any fine-grained material that does not occur in crystalline form. The geochemistry of colloid systems is discussed in detail in sources such as Yariv and Cross (1979) and the references therein.